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A Study of Color Reactions in Non-Aqueous Media.

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A STUDY OF COLOR REACTIONS IN NON-AQUEOUS MEDIA

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TO MY FATHER

whose love, encouragement, advice,
and understanding helped so much
in the completion of this work.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Philip W. West, who directed this research, for his advice and assistance in the completion of this investigation.

He is also indebted to Dr. Clark M. Welch for his helpful suggestions and criticisms and to the Office of Ordnance Research for financial assistance.

He would also like to express his deepest appreciation to his wife for her help and encouragement.

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ABSTRACT

A study of some color reactions in non-aqueous solvents has been made. The major part of the study was concerned with the preparation and reactions of some substituted amides of thioglycolic acid. Compounds of this type show promise for use as analytical reagents. The effect of substitution of nitro groups into N-(phenyl)-mercaptoethanamide was determined and discussed. It was shown that N-(3-nitrophenyl)-mercaptoethanamide might serve very well as a qualitative reagent for cobalt.

It was found that mercury (I) and (II) can be extracted into n-butyl acetate from solutions containing trichloroacetic acid. This may be used to advantage for the detection of small amounts of mercury.

INTRODUCTION

The present investigation was undertaken for the purpose of developing colored chelating agents that might be applied to the detection or determination of inorganic materials in non-aqueous solutions. The development of reagents which give colored chelates, soluble in non-aqueous solutions, would be of value in the detection or determination of inorganic materials especially when combined with extraction procedures.

It is always desirable to have a specific analytical reagent available for a given metal ion. Specificity is not usually attained with the reagent alone, but with a combination of the reagent and proper conditioning agents. A reagent may be made more selective or sometimes even specific by changing its structure while retaining the same functional groupings. Organic reagents having specific or selective action usually react through the formation of inner complex compounds. For the formation of inner complex compounds a reagent must have an acidic group as well as an electron donor atom and these must be situated so as to permit the formation of a 5 or 6 membered ring.

The types of atoms or groups contained in a reagent sometime exert a marked effect on the specificity or

selectivity of the salt formation, as well as on the color and solubility of the salts formed. It is of importance in the search for new organic reagents and their analytical application, and in the improvement of those already in use, that certain groups in organic compounds often have a definite effect on the solubility, color, and stability of the salts formed.

It can be established in many cases that the color and solubility of the salts or organic reagents are dependent on the presence of quite definite atomic groupings. Therefore, such groups can be designated as groups with specific or selective action. However, it must not be forgotten that the reaction conditions, such as control of pH, or selection of solvent, may also exert an important influence on organic reactants. Such effects may sometimes be so great as to give a specific or selective action to a particular grouping simply by control of reaction conditions.

A specific or more selective reaction might be obtained by simply extracting the chelate into a non-aqueous system. Extraction techniques have been used as a valuable tool in analytical chemistry for many years. There have been numerous colorimetric procedures based on the extraction of organo-metallic complexes (30, 36, 37, 41, 45).

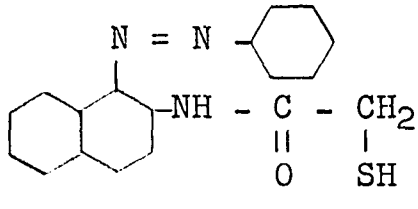
The most familiar type of extraction that is used for analytical work is a liquid-liquid extraction in

which a particular component, usually colored, is extracted into an organic solvent and the intensity of color in the organic phase is measured. The cobalt-thiocyanate complex may be determined in this way by extraction with amyl alcohol (31, 34, 42). Similarly, the iron-thiocyanate complex may be extracted, then measured in an amyl alcohol ethyl ether mixture (46, 49).

There are two principal advantages of using an extraction procedure in colorimetric analysis. First, the desired component often may be separated from colored interferences; and second, small amounts of material can be easily concentrated from relatively dilute solutions. This concentration effect is found in all extraction procedures and is one factor which increases the sensitivity of a reaction.

In this investigation two colored derivatives of N-(2-naphthyl)-mercaptoethanamide (thionalide) were prepared and studied for possible analytical value. Also two nitro derivatives of N-(phenyl)-mercaptoethanamide (thioanilide) were studied for possible use as analytical reagents in non-aqueous systems.

Because the phenylazo and the 1-naphthylazo groups are highly colored, it was decided to introduce them into the one position of thionalide, that is:



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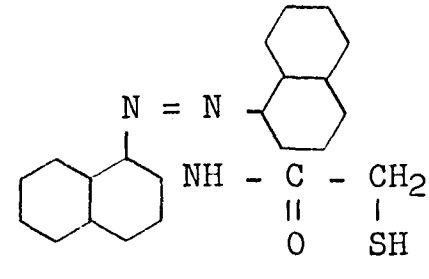


An attempt to make the N-methyl substituted derivative of N-(1-phenylazo-2-naphthyl)-mercaptoethanamide was unsuccessful. Also an attempt to make the p-phenylazo derivative of thioanilide was unsuccessful. The p-nitro and m-nitro derivatives of thioanilide were made but the attempt to make the o-nitro derivative was not successful.

The last part of this dissertation consists of a paper describing the extraction of mercury, which has been accepted for publication and is presented in manuscript form.

REVIEW OF THE LITERATURE

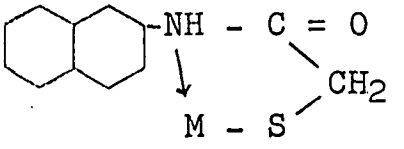
Thionalide was first introduced by Berg et al. (2-7) for use as an analytical reagent. Berg and Roebling (6) report that thionalide precipitates the following metal ions: in sodium hydroxide-tartrate solution, copper (II), silver, gold (III), mercury, cadmium, thallium (I), manganese, and iron (II); in potassium cyanide-tartrate solution, gold (III), thallium (I), tin, lead, antimony, and bismuth; and in potassium cyanide-sodium hydroxide-tartrate solution, thallium (I), mercury, lead, and bismuth. The determination and separation of copper (II), silver, mercury, and bismuth in mineral acid solution has been described by the same authors (7). The limiting concentrations, expressed in micrograms, of reactions with copper (II), silver, gold (III), mercury, tin, arsenic, antimony, bismuth, platinum, and palladium in 0.2 N acid has also been reported by them (5). A specific determination of thallium (I) has been reported by Berg and Fahrenkamp (2, 3).

There have been various methods reported (8, 48, 51, 52) on the preparation of thionalide.

Allan and Beamish (1) have reported the determination of osmium on a micro scale using thionalide. Hoffman et al. (24) has also reported the use of

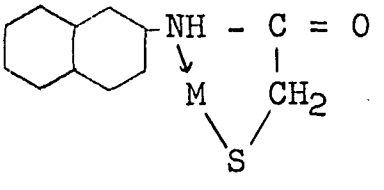
thionalide as a precipitant for osmium. The determination of rhodium using thionalide has been described by Kienitz and Rombock (26) and ruthenium has been determined by Rogers, Beamish and Russell (43).

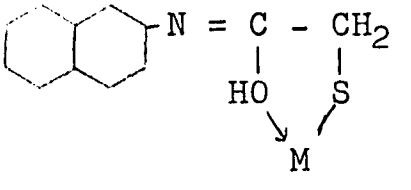
Thionalide forms chelates of the type:

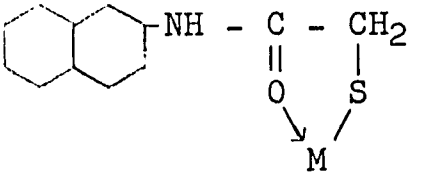


according to Haendler and Geyer (22) where M is a univalent ion. Kubo (28) suggests that thionalide coordinates through the oxygen because of the similarity of the precipitation reactions of o-mercaptobenzoic acid. The author does not agree that this is enough evidence to state that coordination takes place through the oxygen since o-mercaptobenzoic acid will form normal salts, whereas thionalide forms inner-complex salts.

Feigl (19) suggests the following structures as the ones which contribute to chelate formation:

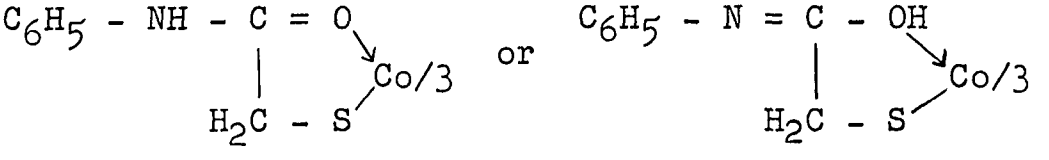




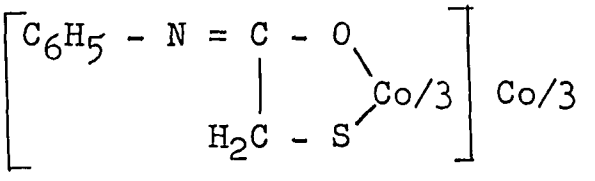


Thionalide is a general reagent reacting with some twenty metal ions. The selectivity of the reagent could probably be enhanced if some alteration of the molecule were made, while retaining the same functional grouping.

Bersin (8) reported using N-(phenyl)-mercaptoethanamide, sometimes called thioanilide, as a test for cobalt. The reactions of this reagent with cobalt and nickel have been studied (8) and it was found that two salts were obtained with cobalt. If the precipitation is carried out at room temperature and the product filtered off at once, a red-brown salt is formed which has a Co:S ratio of 1:3. Higher temperatures and prolonged action of the reagent yield a brown salt with a Co:S ratio of 2:3. The structures proposed for the red-brown salt are:



The brown salt might be represented as:



Buscarón̄s and co-workers (10-13) have prepared two derivatives of thioanilide and have studied them analytically. p-(Mercaptoacetamido)-acetanilide forms precipitates with eight ions (silver, mercury (I), copper (II),

mercury (II), selenium, gold (III), platinum, and rhodium) in acid solution and with five ions (nickel, cobalt, bismuth, thallium (I), and lead) in alkaline solution. The other is o-(mercaptoacetamido)-p-nitrophenol which forms precipitates with silver, mercury (I) and (II), copper (II), arsenic (III) and V, palladium, platinum, gold (III), selenium, bismuth, cadmium, and lead. In ammoniacal solution cobalt and nickel were precipitated, and thallium (I) was precipitated from a potassium hydroxide solution containing cyanide ion.

Weiss (51) has reported the preparation of N-(4-nitrophenyl)-mercaptoethanamide and N-(3-nitrophenyl)-mercaptoethanamide and their gold salts. However, no general analytical study was made by Weiss.

EXPERIMENTAL

A. Apparatus

A Beckman Model DK recording spectrophotometer was used to obtain absorption curves. The solutions were contained in 1.00 cm. silica cells.

All spectrophotometric measurements at a specified wave length were made on a Beckman Model B spectrophotometer using 1.00 cm. Corex cells.

The Sargent Model XI Polarograph was used for the study of the cadmium extraction.

B. Reagents and Solutions

Aniline. The commercial product was purified by distillation.

a-Naphthylamine. The commercial product was purified by recrystallization from warm petroleum ether, Grade B.

All other amines used were Eastman White Label.

a-Mercapto-N-2-naphthylacetamide, Eastman White Label.

All other chemicals used were of analytical reagent grade.

Cadmium Stock Solution. Cadmium metal (0.5024 g.) was dissolved in 5 ml. of nitric acid and 5 ml. of water.

This solution was diluted to the mark in a 500 ml. volumetric flask. The resulting concentration of cadmium was 1005 mg./l.

Cobalt Stock Solution. About 2.9 g. of cobaltous nitrate hexahydrate were dissolved in about 500 ml. of water. This solution was then standardized gravimetrically using a 3% solution of sodium anthranilate. The concentration of cobalt was 1.321 mg./ml. A solution with a cobalt concentration of 132 mg./l. was made up by dilution of the stock solution.

C. Preparations

N-(1-phenylazo-2-naphthyl)-mercaptoethanamide

1. A mixture of 50 ml. of ethanol and 36 g. of 1-phenylazo-2-naphthylamine (23) was refluxed until solution was complete. A mixture of 12 g. of ammonium thiocyanate and 15 g. of chloroacetic acid was added to the amine solution. The solution was refluxed until the mixture hardened to a dark red or black mass. Water was added and the mixture ground until the solid became red. This was filtered with suction and washed with large quantities of water until the filtrate was free of chloride. The filtrate was discarded.

To 18 g. portions of the residue, 400 ml. of methanol, 100 ml. of 28% ammonium hydroxide, 20 ml. water, and 0.15 g. of magnesium ribbon, cut into small pieces, were added and the mixture refluxed for 20

minutes in a stream of nitrogen. Glacial acetic acid was added, still under nitrogen, until the pH was 5-6. The precipitate was filtered off and the filtrate poured into a large volume of water.

The red material was filtered off and dried. It was recrystallized from ethanol-water. The yield was 3.6% and the melting point was 95-6° C.

2. This amide was also prepared using the method reported by Van Allan (48). A mixture of 5 g. of 1-phenylazo-2-naphthylamine (23) and 1.9 g. of thioglycolic acid was dissolved in about 300 ml. of benzene and refluxed for 9 hours using a trap to catch the benzene-water azeotrope as the water was formed, thus preventing it from returning to the pot. The yield was 29% and the melting point was 95-6° C.

N-[1-(1-naphthylazo)-2-naphthyl]-mercaptoethanamide

This amide was prepared by the method reported by Van Allan (48). A mixture of 19 g. of thioglycolic acid and 5.96 g. of 1,1'-naphthylazo-2-naphthylamine (23) was dissolved in about 300 ml. of benzene and refluxed for 9 hours, removing the water as it was formed by means of a trap. The yield was 7% and the melting point was 114-115° C.

N-(1-phenylazo-2-naphthyl)-N-methyl-mercaptoethanamide

The preparation of this amide was attempted using the method reported by Van Allan (48). N-methyl-1-

phenylazo-2-naphthylamine (23) and thioglycolic acid were refluxed in benzene for 9 hours, removing water as it was formed. The product obtained was recrystallized from ethanol-water mixtures and came out in yellow crystals. The melting point was 62-3° C. The yield was extremely small and the product was also very unstable, consequently it had partly decomposed when the carbon-hydrogen and nitrogen determinations were run, therefore the results of the C-H and N were meaningless.

N-(4-phenylazophenyl)-mercaptoethanamide

The preparation of this amide was attempted using procedures reported by Welcher (52) and Van Allan (48). In none of the attempts was there any product corresponding to the amide sought.

The N-(3-nitrophenyl)-mercaptoethanamide and N-(4-nitrophenyl)-mercaptoethanamide were prepared in the same way as reported by Weiss (51). The yields were 9% and 15% respectively.

Every attempt to make N-(2-nitrophenyl)-mercaptoethanamide ended with the recovery of the original amine.

N-(phenyl)-mercaptoethanamide

This amide was made by the procedure given by Welcher (52). The yield was 40% and the melting point was 110-111° C.

D. Procedure and Results

The following procedure was used to determine with which ions the various reagents react. Each ion was tested in acidic, neutral, and basic media. To 1 drop of test solution, which contained 5 mg. ion/ml., 5 drops of water were added and the pH adjusted to about 2,7 or 10. To this, 10 drops of the reagent (0.05% in ethanol) were added and the formation of a precipitate or change of color was noted. The formation of a precipitate generally indicated that a reaction had taken place while a cloudiness usually resulted when the reagent alone separated from solution. These data are shown in Table I.

After precipitation occurred, the solution was extracted with an organic solvent to determine if the precipitate was soluble in the solvent used. The solvent in most cases was n-butyl acetate.

It was observed that N-(3-nitrophenyl)-mercaptoethanamide formed a white precipitate with cadmium in an acidic solution. Since zinc did not form a precipitate, it was believed that this might afford a very good method of separating cadmium and zinc. Consequently, a more detailed study of the efficiency of the extraction was made, using the polarograph to determine the amount of cadmium left after extraction.

Standard curves for polarograph sensitivities of 20, 10, 5, and 1 were obtained using solutions of known cadmium concentration. These curves covered the range of

4.6×10^{-6} to 8.9×10^{-4} molar with respect to cadmium. The cadmium solutions were prepared as follows: to a known amount of cadmium, a few drops of dilute nitric acid and 1 ml. of a 0.05% solution of N-(3-nitrophenyl)-mercaptoethanamide were added. The volume was adjusted to 10 ml. and the solution was shaken with 10 ml. of n-butyl acetate. To a known volume of raffinate, enough potassium chloride and gelatin was added to make the final concentration 0.5 M and 0.01% respectively. The polarogram of the solution was recorded and the concentration of the cadmium was determined from the standard curves. It was found that what at first appeared to be an excellent extraction was most probably a shift of equilibrium and, consequently, only the reagent was extracted. These data are presented in Table II.

It was noted that cobalt formed a red-brown precipitate with N-(3-nitrophenyl)-mercaptoethanamide in an ammoniacal solution and that this precipitate would extract into n-butyl acetate. This extraction was studied with the idea of possibly developing a quantitative method for cobalt. An absorption curve of the complex, dissolved in n-butyl acetate, was obtained on the Beckman Model DK recording spectrophotometer and it was found that the absorption maximum occurred at 480 mu.

It was found, however, that the results obtained from the extraction were neither reproducible nor quantitative. These data are shown in Table III. To determine

if the reproducibility might be a function of the solvent, the following solvents were used: n-butyl alcohol, methyl isopropyl ketone, and mixtures of n-butyl acetate and n-butyl alcohol, n-butyl acetate and methyl isopropyl ketone, and n-butyl alcohol and methyl isopropyl ketone. Since the extraction was not satisfactory in any case, it was concluded that this extraction could not serve as the basis of a quantitative method.

A study of reactions in non-aqueous media was also made using a selected number of ions. This was done by first extracting the ion into a suitable non-aqueous solvent then adding the reagent to the extract. The criteria of a reaction taking place was a change in the absorption of the solution. It was found that these reactions did not offer any convenient method of analysis. These data are shown in Table IV.

The products obtained from the preparation of the phenylazo and naphthylazo derivatives of thionalide were also tested with the metal ions and it was found that in each case apparently only palladium (II) reacted. It was also noted that a solution containing copper (II) and the phenylazo compound gave a lavender lake at a pH of 6 to 9.

These two compounds are new, therefore an elemental analysis was obtained. From three analyses by two companies, three sets of data were obtained, none of which agreed. Although none of the analyses agreed with the theoretical, it is believed that the product obtained

contained some of the compound sought. Although one of the analyses reported no sulfur present, a test for the sulfhydryl group, using sodium azide-iodine solution, was positive. This coupled with the general appearance and reactivity leads the author to believe that at least some of the compound sought was present in the product obtained.

Table I

Color of Precipitates Formed

Ion	N-(3-nitrophenyl)-mercaptoethanamide	N-(4-nitrophenyl)-mercaptoethanamide	Thioanilide
Copper (II)			
acidic	blue	blue	yellow
neutral	blue	NAR*	yellow
basic	blue	NAR	yellow
Gold (III)			
acidic	white	NAR	flesh
neutral	white	brown	flesh
basic	white	NAR	white
Silver			
acidic	yellow	yellow	yellow
basic	yellow	yellow	yellow
Cadmium			
acidic	white	NAR	white
neutral	NAR	NAR	white
basic	NAR	NAR	white
Mercury (I)			
acidic	NAR	yellow	NAR
Mercury (II)			
acidic	white	yellow	white

* No Apparent Reaction

Table I continued

Ion	N-(3-nitrophenyl)-mercaptoethanamide	N-(4-nitrophenyl)-mercaptoethanamide	Thioanilide
Thallium (I)			
neutral	yellow	yellow	yellow
basic	yellow	yellow	yellow
Tin (II)			
acidic	white	NAR	white
Tin (IV)			
acidic	white	NAR	white
Lead			
acidic	NAR	NAR	yellow
neutral	yellow	NAR	yellow
basic	yellow	NAR	yellow
Bismuth (III)			
acidic	yellow	NAR	yellow
Arsenic (III)			
acidic	white	NAR	NAR
neutral	white	NAR	white
basic	NAR	NAR	white
Antimony (III)			
acidic	white	yellow	white
Nickel			
neutral	brown	NAR	brown
basic	brown	NAR	brown

Table I continued

Ion	N-(3-nitrophenyl)-mercaptoethanamide	N-(4-nitrophenyl)-mercaptoethanamide	Thioanilide
Cobalt (II)			
neutral	red-brown	brown	red-brown
basic	red-brown	brown	red-brown
Palladium (II)			
acidic	orange	NAR	orange
neutral	orange	red-orange	orange
basic	yellow	red-orange	orange
Platinum (IV)			
neutral	NAR	red-brown	white
basic	NAR	red-brown	white
Manganese (II)			
neutral	NAR	NAR	white
basic	NAR	NAR	white
Iron (II)			
neutral	NAR	NAR	purple solution
basic	NAR	NAR	purple solution
Iron (III)			
acidic	NAR	NAR	white
neutral	NAR	NAR	olive-tan
basic	NAR	NAR	olive-tan
Ruthenium (III)			
neutral	NAR	NAR	brown
basic	NAR	NAR	brown

Table II

Extraction of Cadmium

Trial	γCd Taken	γCd Remaining
1	1005	1010
2	503	516
3	251	214
4	108	79
5	54	55
6	27	17

Table III

Extraction of Cobalt Complex of

N-(3-nitrophenyl)-mercaptoethanamide

pH 10.0 Solvent: n-Butyl Acetate

γCo Taken	γCo Extracted	O.D. of Complex in Non-Aqueous Phase (480 mu)	% Extraction
66	23.5	0.328	37
66	8.5	0.015	13
66	16.0	0.845	24
66	5.0	0.780	8
132		1.590	
132		1.435	
132		1.540	
26		0.160	
26		0.195	
26		0.218	

Table IV

Reactions in Non-Aqueous Media

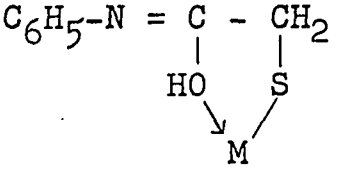
Ion	Addenda and Solvent	N-(3-nitro-phenyl)-mercapto-ethanamide	N-(4-nitro-phenyl)-mercapto-ethanamide
Cu (II)	NCS^- in BuOH*	none	none
Hg (II)	I^- in BuOH	none	none
Pb	I^- in MIK**	none	none
Ni	NCS^- + NH_3 in BuOH	dark yellow	olive brown
Co (II)	NCS^- + NH_3 in BuOH	brown	tan
Pd (II)	NCS^- + NH_3 in BuOH	yellow	yellow
Au (III)	Cl^- in BuOH	none	none

* n-butyl alcohol

** methyl isopropyl ketone

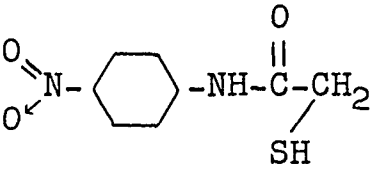
DISCUSSION OF RESULTS AND CONCLUSIONS

Feigl (9) has stated that the C_6H_5-NH-CO-CH_2-SH grouping reacts by coordinating through the oxygen as such or in the enolic form as follows:

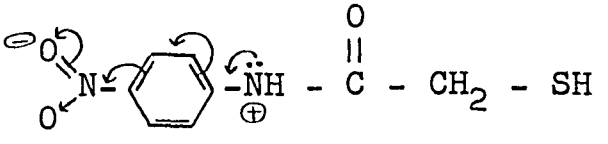


Since nitrogen is a much stronger electron donor than oxygen, the author believes that coordination through the -NH- is predominant.

Consider a molecule of the type



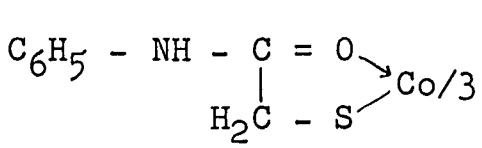
The nitro group is electron withdrawing because of inductive and resonance effects. In the case of the para derivative, it would be expected that the nitro group would deactivate the amide nitrogen. This may be represented by:



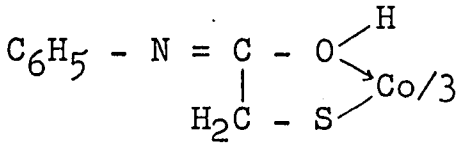
From the above one would expect the nitro group to decrease the reactivity of the reagent, especially if coordination takes place through the -NH- group. Since the nitro group is far removed from the -NH-, the inductive effect should not be too important, but it would also add to the resonance effect.

If the nitro group is oriented meta to the -NH- group, then the resonance effects are virtually eliminated and the inductive effect is the main factor to be considered. One would expect the inductive effect to decrease the reactivity of the reagent, but not as much as the resonance effect does in the para compound. These are substantiated by the fact that the meta derivative reacts with 15 metal ions and the para derivative reacts with 10 metal ions. Thionalide reacts with 20 metal ions. Thioanilide also reacts with 20 ions as reported in Table I.

Bersin has reported that the reaction of thioglycolamide with cobalt yields a red-brown salt that corresponds to structure I or II,

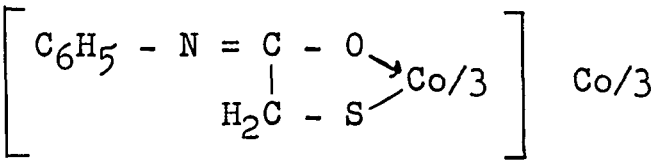


I



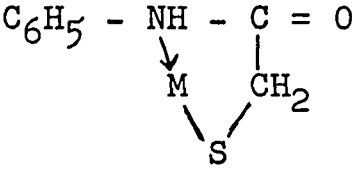
II

and a brown salt that corresponds to structure III.



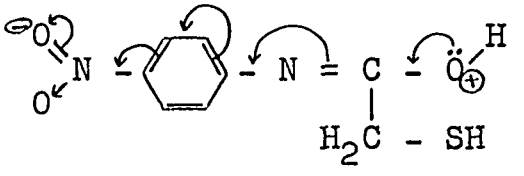
III

The author believes that structure I can be ruled out because substitution of a nitro group in the para position would not affect this type complex formation. Because the effect of substitution is pronounced, the author believes that the coordination takes place through the amide nitrogen as shown in structure IV.



IV

However, this does not rule out the possibility of coordination as in structure II for the resonance effect can be represented by:



and in this case the reactivity will also be reduced.

After finding with which ions N-(3-nitrophenyl)-mercaptoethanamide reacts, it was then decided to study some of the reactions more thoroughly.

A more detailed study was made of the cadmium extraction since cadmium reacted with N-(3-nitrophenyl)-mercaptoethanamide in acidic solution to form a white precipitate while zinc does not react. This appeared to be an ideal method of separating cadmium and zinc. However when a quantitative study of the reaction was made, it was found that the cadmium remained in the aqueous phase. These results are presented in Table II. The reagent is most likely extracted, thus causing a shift in equilibrium, and mere extraction of the reagent is all that is realized.

The extraction of the cobalt complex of N-(3-nitrophenyl)-mercaptoethanamide appeared to be suitable for small amounts of cobalt. However, when solutions of the same concentration were extracted and the optical density of the extract read at 480 mu (which is the absorption peak for the complex), it was found that the extraction was not reproducible. At first it was thought to be because of slight differences in pH, but even after buffering the solution the reproducibility was not improved. The efficiency of the extraction was also determined, and it was found that it varied between 8 and 37%. In determining the efficiency of the extraction, the cobalt was determined by the thiocyanate-acetone method and also with nitroso R-salt. These methods were used to determine how much cobalt was left in the aqueous phase after extraction.

The color of the complex was observed to be very intense in the ammoniacal solution. Qualitatively one may detect one microgram of cobalt per drop easily with the reagent. In this case, however, the test solution is a brown to tan color and a precipitate does not form.

It was then decided to attempt the determination of cobalt in a non-aqueous solvent. The cobalt thiocyanate complex was extracted into amyl acetate and the reagent added. It was found that there was no color development if ammonia was not present and to do the extraction in the presence of ammonia decreased the percentage extraction considerably. Ethylenediamine was tried in place of ammonia but it was not satisfactory.

From this study, it can be concluded that the Ar-NH-CO-CH_2-SH structure offers promise as an analytical reagent. This is especially true of the compounds in which Ar- contains a chromophoric group. A more detailed study of different Ar- groups might lead to some very interesting results at least in the way of selectivity.

It was found that substitution of nitro groups into the aromatic nucleus made the reagent more selective than the parent compound. This might also be accomplished by the introduction of groups which would sterically hinder the reactive site, thus decreasing reactivity. In general, the sensitivity of the nitro derivatives was less than that of the parent compound, although they were

more stable toward oxidation. The nitro derivatives are soluble in alcohol, ether, and various esters, and insoluble in water.

The greatest advantage of carrying out color reactions in non-aqueous solvents is the elimination of interferences. A second advantage is the fact that a colored substance can be determined in the non-aqueous phase directly without reverting to an aqueous determination.

The difficulty of studying reactions in non-aqueous media is the lack of methods of determining a substance in that phase if it is not colored.

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Extraction of Mercury (I) and (II) and
Subsequent Spot Test Detection with Dithizone,
In press, Mikrochimica Acta

EXTRACTION OF MERCURY (I) AND (II) AND SUBSEQUENT SPOT TEST DETECTION WITH DITHIZONE

by
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Dithizone has long been used for the detection of small amounts of mercury. A variety of methods for the detection of this metal in inorganic systems by means of dithizone have been reported (1-12) but all procedures described to date have suffered from numerous interferences because of the well known lack of selectivity of this reagent. The detection of mercury with dithizone in organic material has been reported by Kramerman (13) and Winkler (14, 15). A number of review papers on the general use of dithizone have also appeared (16-20). Miller and Lowe (8) have described the separation of mercury (II) by extraction with ethyl acetate and subsequent detection with diphenylcarbazone. They reported that this method could be applied for the range of 0.25 to 50 milligrams of mercury provided that the extraction was carried out in the presence of hydrochloric acid (about 0.2 M). It was found in the present investigation that the percentage of extraction of mercury (II) was decreased considerably if the chloride concentration was

above 0.1 molar (See Table I). This can account in part for the lack of sensitivity of their test.

A test consisting of an almost specific extraction of mercury by n-butyl acetate in the presence of trichloroacetic acid and subsequent detection with dithizone in the extract is now proposed. The interference of all ions which normally react with dithizone, except gold (III), was eliminated by the use of oxalic acid as a masking agent.

REAGENTS AND SOLUTIONS

Trichloroacetic acid, 3 M aqueous solution.

Oxalic acid, 10 per cent aqueous solution.

Chloroform, analytical reagent.

n-Butyl acetate, CP.

Dithizone, Eastman, White Label, no further purification, 0.002 per cent (wt./vol.) in chloroform.

Mercury (I) stock solution. About 3 g mercury (I) nitrate were dissolved in one liter of distilled water containing 5 ml of nitric acid. This solution was then standardized by titrating the mercury (I) with standard potassium thiocyanate using iron (III) as the indicator. Checks were carried out periodically to determine any change in concentration. The concentration of the stock solution was 2.32 mg mercury/ml. More dilute solutions were made by

taking aliquots of the stock solution and diluting them to an appropriate volume. The concentrations of these solutions ranged from 10 γ/ml to 100 γ/ml. A small drop of metallic mercury was placed in each of the solutions to insure the retention of the mercury (I) form.

Mercury (II) stock solution. 1.179 g of mercury was dissolved in 5 ml of nitric acid and diluted to 250 ml in a volumetric flask. The concentration of the stock was 4.61 mg mercury/ml. Solutions ranging from 10 γ/ml to 100 γ/ml were made up by dilution of aliquots of the stock solution.

EXPERIMENTAL AND DISCUSSION

The general technique followed was to isolate mercury (I) and/or (II) by extracting with n-butyl acetate in the presence of trichloroacetic acid. Dithizone was then added to the extract as a means of detecting the isolated metal. The details are given under PROCEDURE. It was found that in the range of 10 to 100 γ of mercury per 5 ml, the extraction was 89 to 82 per cent complete in a single pass. These data are shown in Table II. When two passes were made using 5 ml n-butyl acetate each time, the efficiency of extraction of 10 γ was increased to 98 per cent. The same results were obtained by using 10 ml of n-butyl acetate in one pass. Chloride ion must

be absent in the extraction of mercury (I) and must not exceed 0.1 M in the extraction of mercury (II). See Table I.

The efficiency of extraction was determined as follows: 5 ml of solution containing mercury ion and trichloroacetic acid were extracted with 5 ml of n-butyl acetate. An aliquot of the raffinate containing from 5 to 15 γ mercury was then placed in a separatory funnel. One drop of concentrated sulfuric acid and 2 ml of 6 M acetic acid were added and the solution diluted to 20 ml. A few milliliters of chloroform were added and the mixture shaken to saturate the raffinate. The chloroform was drawn off and discarded. Five milliliters of 0.001 per cent dithizone in chloroform were added and the mixture shaken for one minute. The optical density of the extract was read at 510 mu using a Beckman Model B spectrophotometer with 1.00 cm Corex cells. The amount of mercury was determined from a standard curve. For the detection of mercury, it was found that the use of a small volume of solution and extracting only once was sufficient to detect as little as 1 γ of mercury.

Interference studies followed the procedure of West (21). In each case, the amount of the interfering ion taken was 500 γ and the amount of mercury taken was 5 γ. The interferences are gold (III), the halides, cyanide, thiocyanate, and sulfide.

PROCEDURE

To one drop of the test solution in a 5-ml beaker, add 10 drops of trichloroacetic acid (3 M), 3 drops of oxalic acid (10 per cent), and 1 ml n-butyl acetate. Mix thoroughly with an extraction pipet and allow the phases to separate. Discard the raffinate, which is the lower layer. Place the extract on a white spot plate and add 2-3 drops of 0.002 per cent dithizone in chloroform. An orange color indicates the presence of mercury.

The limit of identification was found to be 1 γ of mercury in 1 ml of extract.

REMARKS

This method for mercury, although not employing a new reagent, offers a very good way of isolating mercury prior to subsequent identification. The significance of the work lies in the fact that the mercury is extracted from an aqueous solution into an organic phase and is then detected directly in the non-aqueous system. Normal interferences are eliminated by the extraction. It was found that the addition of two drops of a saturated solution of sodium nitrate decreased the time required for the two phases to separate. Solutions of dithizone in n-butyl acetate were found to be relatively unstable, consequently the dithizone should be made up and used in a chloroform solution.

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Table I. Effect of Chloride Ion on Extractability of Mercury (II)

M Cl^-	γHg^{++} taken	γHg^{++} remaining	% Extraction
0.00	100	18	82
0.125	100	20	80
0.25	100	42	58
0.50	100	100	0
1.00	100	100	0
2.00	100	100	0

Table II. Efficiency of Extraction of Mercury (II) in the Presence of Trichloroacetic Acid and Oxalic Acid

γHg^{++} taken	γHg^{++} remaining	% Extraction
100	18.1	81.9
100	18.0	82.0
60	9.0	85.0
20	2.6	87.0
20	2.4	88.0
10	1.1	89.0
10	1.1	89.0
10*	1.1	89.0
10*	1.1	89.0

* Mercury (I) instead of Mercury (II)

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SUMMARY

1. Four substituted amides of thioglycolic acid were prepared and studied for possible use as analytical reagents.
2. The N-(3-nitrophenyl)-mercaptoethanamide showed some promise especially as a reagent for cobalt.
3. An extraction procedure for mercury was developed using trichloroacetic acid and extracting into n-butyl acetate.

VITA

McGee A. Duff was born in Moran, Texas, on August 22, 1926. He received his elementary education in the schools of Moran and Cisco, Texas, and attended high school at Cisco and Sweetwater, Texas, graduating in June of 1943.

He entered Hardin Simmons University for the Summer Session of 1943. He was employed by the Shell Chemical Company from August 1943 to August 1944, at which time he enlisted in the United States Navy. He was Honorably Discharged in June of 1946.

In September, 1946, he entered Southern Methodist University and completed his B. S. degree in June, 1950. He entered the Graduate School of Southern Methodist University the fall of 1950. On June 30, 1951, he married Patricia Gene Johnson. He received his M. S. degree from Southern Methodist University in June of 1952.

He entered the Graduate School at Louisiana State University in September, 1952. He has held a Research Fellowship sponsored by the Office of Ordnance Research for the years 1953-55. A son, Tommy Caleb, was born on March 17, 1954.

He is now a candidate for the degree of Doctor of Philosophy.

EXAMINATION AND THESIS REPORT

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Major Field: Chemistry

Title of Thesis: A STUDY OF COLOR REACTIONS IN NON-AQUEOUS MEDIA

Approved:

Philip W. West
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Richard J. Russell
Dean of the Graduate School

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